ELECTROCHEMICAL DETECTION OF IODOPHENOLS AT BORON-DOPED DIAMOND THIN-FILM ELECTRODES

Audrey N. Martin and Greg M. Swain

Department of Chemistry, Michigan State University, East Lansing, MI 48824

Keywords: iodophenol, water disinfection, boron-doped diamond

Abstract

Currently there is little on-line monitoring capability onboard the International Space Station (ISS) for water quality management. Water quality is presently monitored by periodically returning samples to earth; consequently, there is no way to promptly respond to a contamination outbreak. In the past, water samples were regularly returned for analysis by the Space Shuttle, however, since the Columbia accident, water samples have not been regularly brought back for analysis. Therefore, water quality monitoring has become a major concern for the National Aeronautic Space Administration (NASA). Water disinfection can be accomplished by introducing iodine (I_2), taking advantage of its biocidal and virucidal properties to purify the water supply. Concerns have been raised about the possibility that I_2 could react with aromatic contaminants reclaimed from the shuttle condensate to form iodinated aromatics.[1] Although the toxicity of iodinated aromatics is unknown, it is hypothesized that they possess toxicity similar to that of their chlorinated counterparts, such as chlorophenol.

This research is focused on development of an electrochemical detection scheme for iodinated phenols using boron-doped diamond (BDD) electrodes. Electrochemical detection of waterborne contaminants is relatively simple, inexpensive, and utilizes small and easy to operate instrumentation. The most important component of any electrochemical detection system is the electrode material. BDD thin-film electrodes are appealing because of their (i) wide potential window, (ii) minimal pretreatment for activation, (iii) stable morphology and microstructure in harsh chemical environments, (iv) stable and low background current, (v) and weak adsorption of polar molecules on the hydrogen-terminated surface (i.e., resistance to fouling). These qualities are especially appealing to the detection of phenolic compounds because their oxidation potentials approach that of oxygen evolution on many electrode materials and phenolic reaction by-products can polymerize and adsorb on (foul) the electrode surface. Boron-doped diamond electrodes have previously been used for the detection of chlorinated phenols and have been shown to be an ideal electrode material in terms of electrochemical activity and response stability.[2]

The feasibility of BDD electrodes for the oxidative detection of iodinated phenols was investigated. 2-iodophenol (2-IP), and 4-iodophenol (4-IP) in phosphate buffer (pH 3.5), and 2,4,6-triiodophenol (TIP) in acetonitrile/phosphate buffer (pH 7.1) were characterized with microcrystalline boron-doped diamond thin-film electrodes using cyclic voltammetry and flow injection analysis (FIA) with amperometric detection. The decreased solubility of TIP necessitated the use of the mixed buffer solution. Characteristics, such as the electrode response, reaction products, and fouling resistance, were investigated. The mechanism for phenol oxidation has been extensively studied[3] and it is hypothesized that the iodophenol oxidation follows the same mechanism. Figure 1 shows the typical cyclic voltammetric i-E curve for 2-iodophenol at a BDD microcrystalline electrode. During the first scan, only the oxidation peak is observed for the oxidation of 2-IP to the iodophenoxy radical (peak A). The radical can then either (i) polymerize or (ii) be further oxidized to form quinone-like compounds, which are then reduced on the reverse sweep (peaks B and C). The shoulder on peak C is assumed to be associated with the reduction of a dissolved quinone-like species. Subsequent scans show two additional oxidation peaks, D and E, which are associated with the species formed during the reduction at peaks B and C. The oxidation current near 0.9 V (peak A) decreases to a point with cycling, while the reduction currents near 0.15 V and 0.5 V increase (peaks B and C). This leads to the hypothesis that oxidation reaction products adsorb on the electrode surface and block some electrochemically-active sites. Similar phenomena were seen during the electrochemical detection of chlorinated phenols.[2] 4-IP and TIP show similar electrochemical behavior to 2-IP at microcrystalline diamond.

FIA was used to study the electrochemical response of iodophenols on BDD. FIA allows for an on-line method of detection that serves as a very basic prototype for a constant monitoring system. It is hypothesized that the constant movement of solution through the flow-cell will reduce the rate of electrode fouling. Preliminary studies with 2-IP show the ideal detection potential for FIA of 2-IP is 950 mV vs. Ag/AgCl. After stabilization, a current of 8.5nA was measured. The analytical figures of merit of 4-IP and TIP will also be presented.

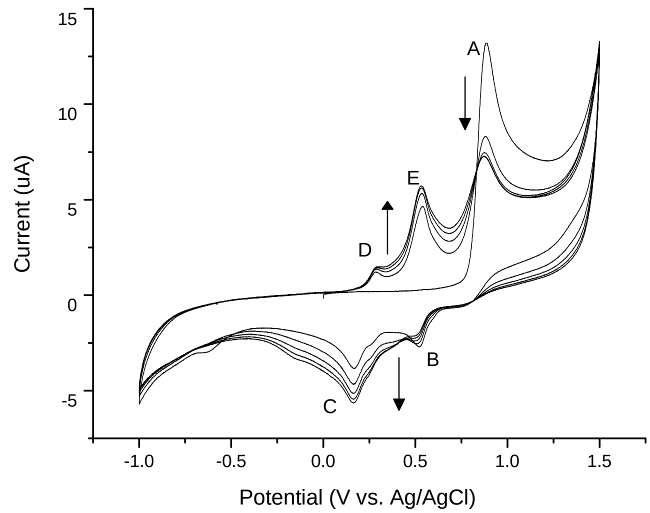

Figure 1. Cyclic voltammetric i-E curve for 0.1mM 2-iodophenol in 0.1M phosphate buffer, pH 3.5 at a microcrystalline BDD thin-film electrode. Scan rate: 100mV/s, Electrode area: 0.2cm^2.

REFERENCES

1. Dietrich, A.M., et al.: "Flavor Profile Analysis and GC/MS Detection of Phenolic Iodinated Disinfection Byproducts in Drinking Water for the USA Space Program," *Wat. Sci. Tech.*, Vol. 40, No. 6, 45-51 (1999).

2. Muna, G.W.; Tasheva, N.; and Swain, G.M.: "Electro-oxidation and Amperometric Detection of Chlorinated Phenols at Boron-Doped Diamond Electrodes: A Comparison of Microcrystalline and Nanocrystalline Thin Films," *Environ. Sci. Technol.*, Vol. 38, No. 13, 3674-3682 (2004).

3. Gattrell, M. and Kirk, D.W.: "A Study of the Oxidation of Phenol at Platinum and Preoxidized Platinum Surfaces," *J. Electrochem. Soc.*, Vol. 140, No. 6, 1534-1540 (1993).